

IV.C.2 HyMARC (Core): LLNL Effort

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Overall Objectives

- Accelerate discovery of breakthrough storage materials by developing foundational understanding of phenomena governing the thermodynamics and kinetics limiting the development of solid-state hydrogen storage materials.
- Develop community tools and capabilities to enable materials discovery, including computational models and databases, new characterization tools and methods, and tailorable synthetic platforms.
- Provide technical direction to HyMARC via leadership of Task 2 (Mass Transport) and coordination of theory efforts.
- Provide new computational models for hydrogen interactions in hydrides and sorbents.
- Provide tailored porous aerogel materials for sorbents and encapsulants.
- Provide characterization of hydrides and sorbents using soft X-ray absorption and emission spectroscopy.

Fiscal Year (FY) 2017 Objectives

- Develop computational methods for more accurate thermodynamics of hydrides and their interfaces.
- Investigate mass transport in complex microstructures in metal hydrides.
- Establish computational framework for solid mechanics and confinement effects on reaction enthalpies.
- Understand H_2 interactions with model sorbents and catalysts.

- Establish synthetic protocols for incorporating dopants into graphene aerogels.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (A) System Weight and Volume
- (E) Charging/Discharging Rates

Technical Targets

This project will develop foundational understanding and new capabilities that will enable accelerated discovery of breakthrough materials in all classes of storage materials, in particular metal hydrides and sorbents. It is anticipated that the insights gained from this research, coupled with new synthetic, characterization, modeling, and database tools that will be made available to the hydrogen storage research community, will lead to materials that meet DOE system targets such as gravimetric and volumetric capacity, system fill time, delivery temperature, and cost.

FY 2017 Accomplishments

- Established synthetic protocols for B/N doping of graphene aerogels for hydride infusion and direct sorption testing.
- Improved free energy predictions of hydrides by considering explicit thermal effects, with results tested and successfully validated on a Mg-B-H system.
- Predicted stability trends of B_xH_y intermediates beyond the bulk crystalline limit to understand reaction pathways under non-equilibrium reaction conditions.
- Developed new theory capability to quantify the destabilizing effect of internal and external stress on reaction enthalpy due to volume expansion upon hydrogenation.
- Demonstrated new computational methods for non-equilibrium mass transport in complex microstructures.
- Performed reactive ab initio molecular dynamics simulations of MgB_2/H_2 and MgB_2 /etherate interfaces to elucidate local reaction mechanisms and coordination complexes.

- Examined thermodynamic, kinetic, and electronic effects of TiF_3 catalysts via first-principles calculations.



INTRODUCTION

Storage of hydrogen onboard vehicles is one of the critical enabling technologies for creating hydrogen-fueled transportation systems that can improve efficiency, enhance resiliency, and encourage independence of the national energy infrastructure. Stakeholders in developing hydrogen infrastructure (e.g., state governments, automotive original equipment manufacturers, station providers, and industrial gas suppliers) are currently focused on high-pressure storage at 350 bar and 700 bar, in part because no viable solid-phase storage material has emerged. Nevertheless, solid-state materials, including novel sorbents and high-density hydrides, remain of interest because of their unique potential to meet all DOE Fuel Cell Technologies Office targets and deliver hydrogen with lower storage pressures and higher onboard densities. However, the existing materials suffer from thermodynamic and kinetic limitations that are often poorly understood, which prevent their application as practical H_2 storage media.

APPROACH

HyMARC seeks to address these gaps by leveraging recent advances in predictive multiscale modeling, high-resolution in situ characterization, and novel material synthesis techniques. By focusing on the underlying thermodynamic and kinetic limitations of storage materials, we will generate foundational understanding that will accelerate the development of all types of advanced storage materials, including sorbents, metal hydrides, and liquid carriers. LLNL objectives and responsibilities within HyMARC include (1) providing technical leadership for Task 2 (Mass Transport) and coordinating all theory efforts; (2) providing computational methods for more accurate prediction of sorbent and hydride thermodynamics; (3) developing tools for multiscale modeling of hydride kinetics, including mass transport, chemical kinetics, and phase kinetics; (4) synthesizing carbon frameworks and sorbents with tailored porosity and chemistry; and (5) support HyMARC characterization efforts surrounding soft X-ray spectroscopy.

RESULTS

Sorbent synthesis: A key goal of our synthesis efforts is the development of protocols for making tailored graphene aerogels that can be chemically optimized via B and N doping. We prepared B-doped and N-doped graphene aerogels by thermal treatment of graphene aerogels in the presence of a B or N precursor. Graphene aerogels were

immersed in a solution of the precursor and freeze dried, then the composite was thermally annealed at elevated temperatures ranging from 1,000–2,000°C. The annealed samples were then submitted for compositional analysis by X-ray photoelectron spectroscopy. B and N lattice incorporation was confirmed at levels of up to 2.7 at% for B and 2.0 at% for N. We have found success using two approaches, boron oxide incorporation plus annealing for B doping and melamine incorporation plus annealing for N doping. However, we are still trying to increase the overall doping levels, as well as to increase chemical purity. For instance, B doping tends to also introduce N, possibly due to the conditions for the carbonization process. This suggests the need to investigate different gel formation precursors for B and N doping that may be able to introduce higher dopant concentrations.

Free energies of complex metal hydrides: We have implemented improved ab initio thermodynamics computations of hydrides, focusing on the use of ab initio molecular dynamics as a tool for obtaining more accurate free energies of the complex metal hydride systems as a function of temperature and composition. Our improved ab initio thermodynamics captures full dynamical contributions from both quasi-harmonic and anharmonic vibrations, and we applied our strategy to the Mg-B-H system as an example and evaluated the significance of anharmonicity.

As shown in Figure 1a, the differences between the standard enthalpy (zero-K intercepts, including zero-point energy contributions), the free energy within the harmonic approximation (dashed lines), and fully dynamical free energy descriptions (solid lines) are rather dramatic, particularly at high temperatures. The origin of this difference can be traced to the molecular reorientations and soft vibrations of the complex anions, which have significant anharmonic contributions that are not captured by conventional treatments. This fundamentally alters the predicted thermodynamics under the extreme conditions of dehydrogenation, having a large stabilizing influence on intermediates like $\text{MgB}_{12}\text{H}_{12}$ and $\text{Mg}(\text{B}_3\text{H}_8)_2$ that have major anharmonic molecular contributions. Notably, these results suggest the need to revisit earlier thermodynamic computations of all complex metal hydrides, which differ from conventional simple and interstitial metal hydrides in the relevance of the complex anion dynamics. Although ab initio molecular dynamics carries significant computational expense, the more accurate free energies obtained by these computations will serve as a far more reliable basis to investigate potential engineering strategies, such as changes in particle size or the introduction of mechanical stress induced by a confinement medium.

Stability of B_xH_y intermediates in metal borohydrides: In the Mg-B-H system, our thermodynamic free energy predictions in Figure 1a qualitatively agree with those of Zhang et al. [1] in that they do not predict stable formation

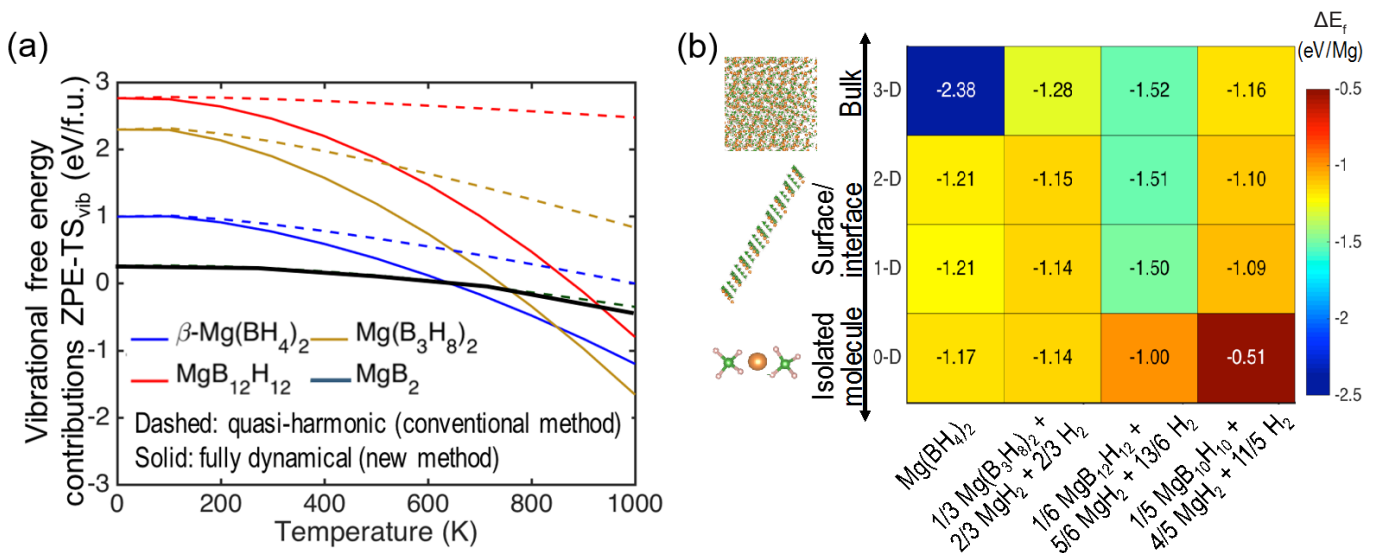


FIGURE 1. (a) Calculated thermal energy contributions from the quasi-harmonic approximation (dashed lines) and full ab initio molecular dynamics including anharmonicity (solid lines) for various compounds in the Mg-B-H system. (b) Mass-balanced formation energies of MgB_xH_y compounds as isolated molecules (0-dimensional), lines and planes of molecules that are more representative of surfaces and interfaces (1-D and 2-D), and bulk materials (3-D).

of MgB_xH_y intermediates other than MgB₁₂H₁₂. However, several other chemical intermediates have been observed experimentally, most commonly via ¹¹B nuclear magnetic resonance [2–4]. Assuming moderate accuracy of density functional theory (DFT) as a computational tool, we are left to conclude one of four possibilities: (1) another as-yet-undiscovered structure exists, causing us to miscalculate the thermodynamics; (2) the intermediates are kinetically stabilized; (3) the intermediates exist not as solid phases but as chemical species whose energetics depend on their solid-state environment; or (4) the amorphous nature of the intermediates alters their relative thermodynamics. In the effort to address the last two possibilities and gain qualitative insights into how intermediate stability might change in an amorphous state or as a molecular or polymeric species at a solid-solid interface, we modeled the morphology-dependent stability of Mg-B-H compounds by considering the chemical bond properties more explicitly.

Specifically, the stability of molecular complexes at interfaces were estimated by considering the formation energies as a function of *dimensionality*. These values are shown in Figure 1b. The 0-dimensional case represents the isolated molecular complexes of the proper stoichiometry in the gas phase, for example an Mg(BH₄)₂ molecule, whereas the 3-dimensional (3-D) reference case is for the crystalline bulk material. In 1-dimensional (1-D) and 2-dimensional (2-D), the MgB_xH_y molecules are arranged in a chain and in a plane, respectively. These 1-D and 2-D configurations are broadly representative of how the molecules might coalesce in interfacial or surface layers. The results in Figure 1b show that Mg(BH₄)₂ is significantly more stable

(>1 eV) when condensed in the 3-D crystal, as expected. However, Mg(B₃H₈)₂, MgB₁₂H₁₂, and MgB₁₀H₁₀ become competitive with Mg(BH₄)₂ when coordinated in lower dimensions. Particularly, for MgB₁₂H₁₂ the energy penalty incurred to form 1-D chains or 2-D sheets from 3-D bulk is negligible, since most of its energy stabilization lies in the chemical stability of the closoborane B₁₂H₁₂²⁻ unit and in its ionic interaction with Mg²⁺, which do not depend on the dimensionality. In fact, the formation energy of MgB₁₂H₁₂ in 1-D and 2-D is even lower than that of Mg(BH₄)₂, suggesting it could be the preferred species at a solid-state interface and could nucleate easily in this environment. This new dimension-dependent energy analysis could be a powerful tool for understanding the stability of borohydride intermediates, as well as devising strategies for relative destabilization of competing products.

Mass transport at surfaces and through complex hydride microstructures: Our theory effort to model the mass transport within a realistic material microstructure with structural inhomogeneities has focused on two activities. First, we established a computational framework to model full 2-D hydrogen transport on a surface (e.g., during a spillover hydrogenation process). This multiscale capability simulates the long-range and long-time mass transport behavior by coupling the atomistic jumping mechanism to a continuum diffusion model.

We applied this extended simulation capability to the hydrogen refilling and redistribution process within a cleared region on Mg(0001) surface, which emulates the low-energy ion scattering experiments being performed by HyMARC partners. The relevant surface diffusivity tensor

were derived from kinetic Monte Carlo based on barriers from DFT combined with geometric analysis of diffusion pathways. Using the derived surface diffusivity tensor, we next numerically solved the continuum diffusion equation for hydrogen refilling via surface diffusion into pre-cleared regions. Resulting refilling rates for pre-cleared areas with different initial geometries (but identical areas) are compared in Figure 2a. Monitoring the hydrogen concentration at the center of the cleared region, the simulation results verify that the refilling kinetics depends strongly on the geometry. By coupling upcoming low-energy ion scattering experiments with corresponding surface diffusion simulations, we can more precisely determine the hydrogen surface diffusion coefficients and mechanisms. With proper parameterization, the method may also be extended to model the chemically reactive structural diffusion in complex hydrides.

Second, we established an efficient mesoscale computational method for extracting the effective diffusivity of an inhomogeneous microstructure containing multiple grains and phases. Synthesized hydrides for hydrogen storage are typically highly polygranular, and a complex variety of additional intermediate phases appears during (de)hydrogenation. As a result, metal hydrides exhibit complex microstructures under operating conditions. Obviously, the diffusion properties of such microstructures with multiple grains in different orientations, multiple phases in different crystal structures, and a complex grain and phase boundaries network would deviate from those of a pristine single crystal. To address this challenge, we integrated the atomistically derived bulk and surface diffusivity tensors with an established computational method for extracting the effective diffusivity of an inhomogeneous and complex microstructure containing multiple grains and grain boundaries.

Using hydrogen diffusivity tensors of bulk and surface Mg derived from the kinetic Monte Carlo approach

mentioned above, we extracted the effective diffusivities of a polycrystalline grain structure (see the inset of Figure 2b) for several temperatures. Figure 2b shows the computed results along with the bulk and surface diffusivities for comparison. The results show that the effective diffusivities have activation barriers that are dominated by bulk behavior at higher temperatures and surface behavior at lower temperatures. Encouraged by this successful demonstration, we can now systematically investigate the relationship between diffusion properties and microstructural features and topology.

Mechanical stress effects on hydride enthalpy:

Mechanical stresses, whether induced intrinsically from the growth of a product phase with significant associated volume change or else extrinsically imposed by a confining medium, can play a significant role in determining the thermodynamics and kinetics of phase transformations of hydrides. Residual stresses upon cycling are also closely related to the material fatigue and fracture, and can limit cycle life of a hydride. To predict the mechanical stress effects arising from crystallographic structural changes and/or volume expansion during solid-state phase transformations of metal hydrides with or without an confining medium, we have begun with the Mg-H system as a model of a simple hydride.

Our methods are based on a multiscale approach borrowed from the metallic alloy phase transformation community [5,6], which integrates microelasticity theory in continuum mechanics with first principles-derived materials parameters. First, we derived the associated transformation strain matrix, which connects the crystallographic planes of the product and reactant phases. Due to the crystallographic symmetry changes associated with the Mg (*hcp*)-to-MgH₂ (*bct*) phase transformation, the system exhibits “multi-variant” characteristics, meaning it has multiple symmetry-

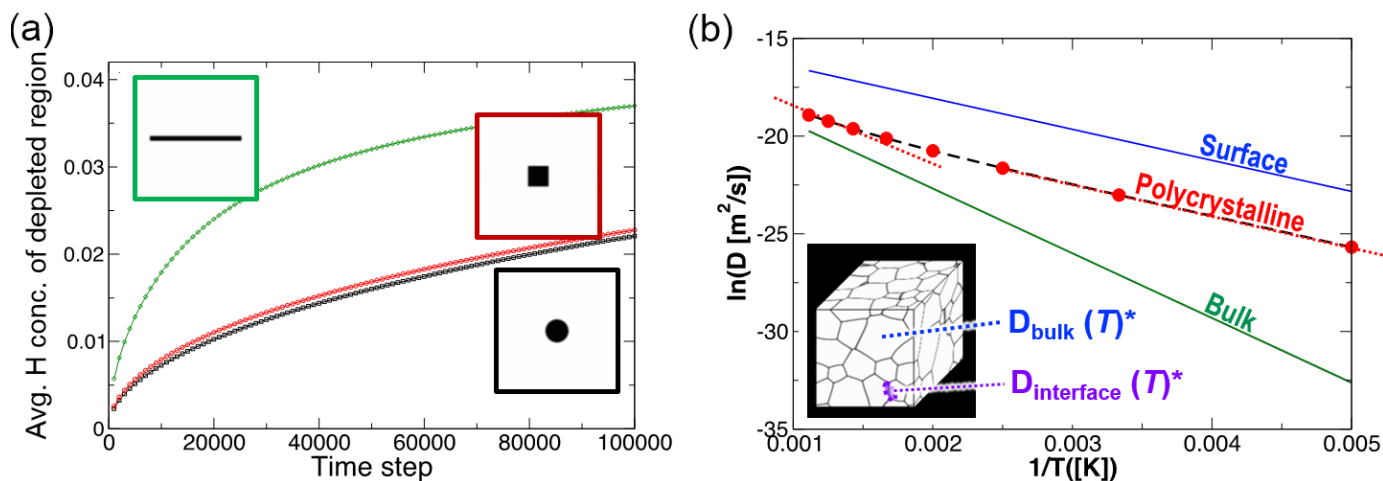


FIGURE 2. Multiscale computational modeling approach for (a) simulating surface diffusion of H on Mg(0001) surface after local depletion in regions with different geometries and (b) extracting effective diffusivities of H in polycrystalline Mg.

equivalent possible distortion orientations. Using the lattice parameters and elastic moduli for each phase as computed with DFT, deformation matrices and lattice mismatches between the two phases were derived.

The Mg to MgH₂ phase transformation involves a significantly large (~30%) volume change. If we consider the formation of MgH₂ created within an Mg matrix under volumetric constraint, this volume mismatch is predicted to have an unrealistically large value of elastic energy (~35 GPa). We can therefore safely assume that the system will introduce interfacial dislocations and other defects at the Mg/MgH₂ boundary. This phenomenon, known as “coherency loss,” relaxes the elastic energy. In complex hydrides, the volume change upon hydrogenation is often far greater than in the Mg/MgH₂ system; thus, it is reasonable to assume that this same coherency loss condition is universal to non-interstitial metal hydrides. Following a method we recently developed and published [7], we explored the possibility of coherency loss by introducing factors (m, n) that describe the density of dislocations incurred along each of the two lattice-unique crystallographic directions in Mg and MgH₂. Then, the characteristic strain energy variations for possible coherency states were computed and confirmed that the strain energy magnitude is highly sensitive to the interfacial coherency state (i.e., dislocation density) as expected. For instance, the elastic strain energy is reduced from 35 GPa in the fully coherent case to 1.5 GPa for a dislocation density of ~40%. This strongly implies that the interfaces exhibit significant coherency loss in the Mg/MgH₂ system, and gives a better picture of the actual disordered structure of the interface.

The same approach was also used to calculate the characteristic internal strain energy in confined Mg associated with external stress imposed by the confining medium. To do so, a (de)hydrogenating Mg particle in a confining medium was constructed and modeled as assembled segments with bi-axially compressed thin film geometries in different crystallographic orientations (assuming a core-shell geometry; see Figure 3a). As shown in Figure 3b, the resulting computed elastic strain energy arising from the external volumetric confinement depends on the crystallographic orientation, as expected from the symmetries of the parent phases. If we average over all orientations to obtain the average strain energy for the entire particle, we predict that volumetric constraint can destabilize MgH₂ with respect to Mg by ~8.2 kJ/mol H₂. This agrees extremely well with a relative destabilization of 8.1 kJ/mol H₂ measured by our HyMARC partners via pressure-composition-temperature analysis of Mg/MgH₂ confined in reduced graphene oxide [8]. The excellent agreement suggests that mechanical stress effects may largely account for the observed changes the reaction thermodynamics for confining media with different stiffness and pore geometry, thereby altering the stabilities of hydrides during (de)hydrogenation.

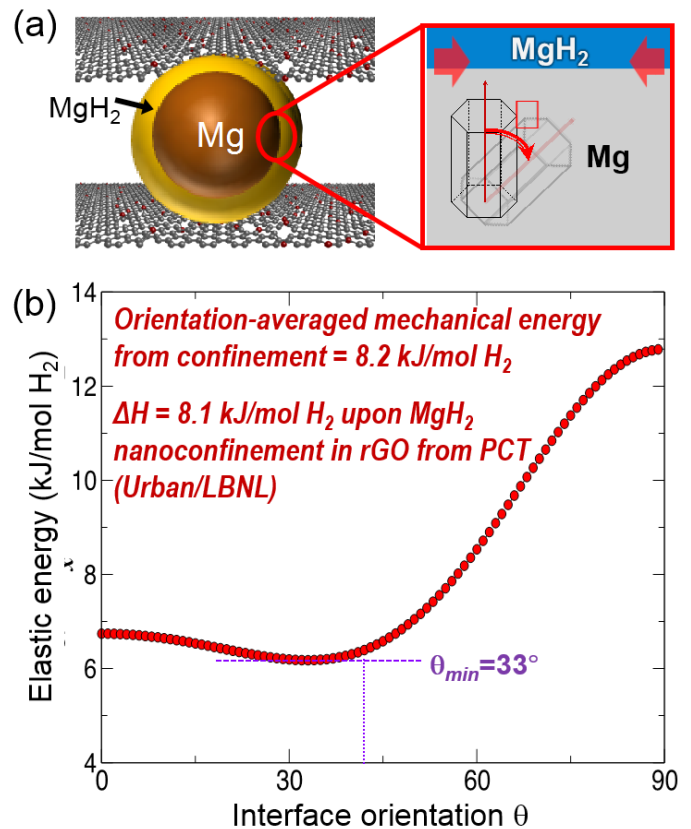


FIGURE 3. (a) Schematic of the orientation-dependent mechanical stress effect at Mg/MgH₂ interfaces in our multiscale micromechanical approach. (b) The calculated orientation-dependent elastic energy affecting the reaction enthalpy of an Mg-H particle in a confining medium.

Surface interaction of H₂ with model catalyst additives:

Although TiF₃ and TiCl₃ are often added as catalysts in a wide variety of metal hydrides, their activity mechanism has not been well understood. A first step is to understand whether the additives themselves are inert to hydrogen, which would verify that their activity instead relies on incorporation into other reaction materials. This would also establish whether Ti can act as a dissociation catalyst in these materials—one of its many proposed roles. X-ray absorption spectroscopy performed by HyMARC partners recently established that pure TiF₃ and TiCl₃ phases without metal hydrides are not intrinsically reactive to H₂, but only become so upon interaction with the active material. To better understand the origin of these results, we performed additional DFT-based theoretical investigations of catalytic reactivity of TiF₃ by computing hydrogen dissociation energetics and barriers on TiF₃ surfaces.

If we assume the presence of surface fluorine vacancies to form binding sites for H₂, then dissociative adsorption on TiF₃ is found to be energetically favorable (e.g., by -0.18 eV/H₂ for the reaction shown in Figure 4). However,

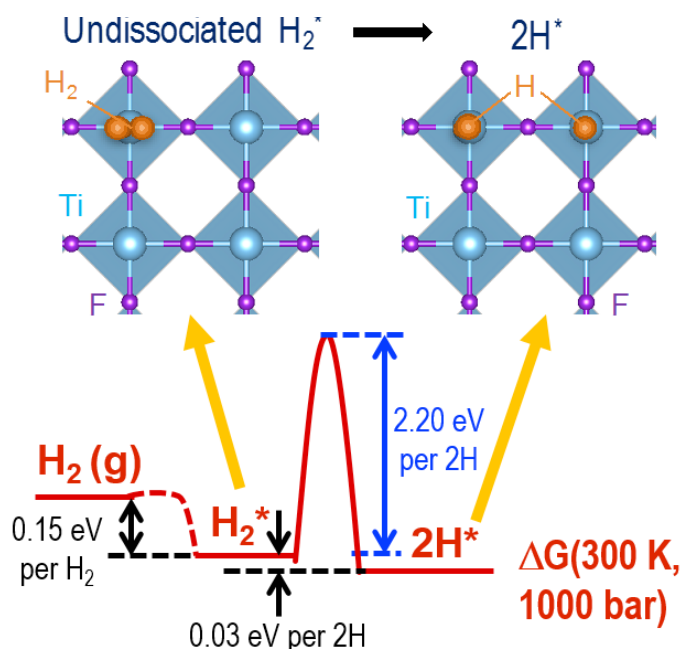


FIGURE 4. Illustration and full energy landscape for one possible H_2 dissociative adsorption reaction on the surface of TiF_3 when outermost surface F atom sites are vacant.

the dissociation energy barriers computed in DFT nudged elastic band calculations were found as high as 2.18–2.21 eV, leading us to conclude that TiF_3 is intrinsically inactive as a catalyst towards H_2 . It is worth noting that these thermodynamic driving forces and kinetic energy barriers are highly influenced by the local environment of surface Ti, most notably, by the number and arrangement of surrounding F atoms. By systematic computation of the driving forces and energy barriers as a function of the coordination number of F around surface Ti, we found that the catalytic reactivity observed in experiments when TiF_3 is ball milled with hydrogen storage systems can be understood by one or more of following possibilities. First, different phases, phase morphologies, or chemical species that are reactive towards H_2 may form when TiF_3 is dissociated upon mixing and incorporates directly into the active material. This possibility is widely assumed in the literature. Second, some Ti may remain as TiF_3 , but they become highly under-coordinated as F atoms are stripped due to mechanical erosion during ball-milling. Such highly under-coordinated Ti (e.g., Ti with two neighboring F vacancies in TiF_3) could in principle be reactive towards H_2 . Third, Ti coordination in TiF_3 may be significantly altered at interfaces by placing it in direct contact with the active material. In this case, H_2 (or atomic H) may simultaneously interact with the TiF_3 catalyst material and the active material, possibly lowering the energy barrier for dissociating H_2 .

CONCLUSIONS AND UPCOMING ACTIVITIES

Our team has interacted closely with the other HyMARC partners and new seedling projects to build foundational understanding of thermodynamics and kinetics in solid-state hydrogen storage materials. This year, our synthetic efforts on porous carbon sorbents have mostly focused on boron and nitrogen incorporation. On the characterization side, we have continued our investigations into materials changes upon hydrogenation using soft X-ray probes in collaboration with the other HyMARC labs. On the theory side, we have prioritized development of new computational frameworks for improving the accuracy and realism of complex materials simulations for hydrogen storage. For instance, we showed that the accuracy of hydride thermodynamics computations could be improved using explicit thermal effects taken from ab initio molecular dynamics, suggesting previous first-principles calculations of hydride thermodynamics should be revisited. We also developed a formalism for introducing solid mechanics and interfacial effects in thermodynamic computations, and showed excellent agreement with measured data on the reaction enthalpies of nanoconfined Mg/MgH₂. Furthermore, we performed detailed studies examining the interaction of hydrogen with surfaces in catalysts and sorbents that provide additional insights into the functionality of these materials in (de)hydrogenation reactions. In the coming months, we will:

- Continue our computations of entropy effects and free energies of the remaining borohydride systems.
- Investigate confinement effects in the Mg-B-H and Na-B-H systems using first-principles computations and solid mechanics.
- Use theory to investigate the surface chemistry of complex hydrides in the presence of oxide contamination.

SPECIAL RECOGNITIONS & AWARDS/PATENTS ISSUED

1. Urban, J.J., Ruminski, A.M., Cho, E.S., Bardhan, R., Brand, A., Wood, B.C., Heo, T.W., Shea, P.T., Kang, S., and Zhou, X., “Hierarchically Controlled Inside-Out Doping of Mg Nanocomposites for Moderate Temperature Hydrogen Storage,” U.S. Provisional Patent #62/445,610 (2017).

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7. K.G. Ray, “X-ray absorption and emission spectroscopy of the initial hydrogenation of MgB_2 ,” Advanced Light Source User Meeting, Berkeley, CA, October 2016 [invited].
8. S. Kang, “Beyond-ideal modeling of (de)hydrogenation in complex metal hydrides,” International Symposium on Hydrogen Energy, Waikoloa, HI, February 2017 [invited].
9. S. Kang, “Thermodynamics and Kinetics at Interfaces of Metal Hydrides for Hydrogen Storage,” American Chemical Society Meeting, San Francisco, CA, March 2017.
10. T.W. Heo, “Multiscale modeling of solid-state phase transformations in metal hydrides for hydrogen storage,” Materials Research Society Spring Meeting, Phoenix, AZ, April 2017.
11. T.W. Heo, “Mesoscale modeling approaches for hydrogen generation and storage,” Electrochemical Society Meeting, New Orleans, LA, May 2017 [invited].
12. S. Kang, “Challenges and opportunities for interface modeling in metal hydrides for hydrogen storage,” Electrochemical Society Meeting, New Orleans, LA, May 2017.
13. B. Wood, “Predicting properties of complex interfaces for hydrogen production and storage: Challenges and strategies,” Electrochemical Society Meeting, New Orleans, LA, May 2017 [invited].
14. B.C. Wood, “Complex dynamics in metal borohydrides: From hydrogen storage to solid-state batteries,” Gordon Research Conference on Hydrogen-Metal Systems, Easton, MA, July 2017 [invited].
15. S. Kang, “Multiscale modeling of interfaces in metal hydrides,” Gordon Research Seminar on Hydrogen-Metal Systems, Easton, MA, July 2017.

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